Combinatorial Test of Polymer Craze Growth and Fracture

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The fracture properties of polymer films are critical to coatings applications and highly susceptible to influences of geometry, polymer structure and formulation. The copper grid test, a well-established method of producing isolated crazes in sub-regions of glassy polymer films, has been extended to accommodate gradient thin film libraries. This enables systematic study of multiple parameters influencing these load-bearing, pre-crack structures. AFM has been used to image and quantitatively characterize structure at both the tip and midsections of crazes in polystyrene films as thin as 50 nm.

The method of using an annealed, ductile copper grid to support and deform thin polymer films was developed more than 20 years ago. Since that time, it has been used primarily in fundamental studies of the nature and origin of crazes in glassy polymer films. Most of the films that have been studied were uniform compositions of homopolymers and the multiple grid squares were used for statistical validation. It is also well known, however, that the fracture properties of thin polymer films can be drastically altered with additives such as those commonly used in formulation science as well as by changing the basic molecular characteristics of the base polymer (i.e. molecular weight, tacticity, etc.) relating to mobility in the film. The gradient film techniques being developed at NIST combined with this existing test enabled us to carry out a single test in which some of these critical factors could be varied systematically over one film.

To validate the combination of the two approaches, the effects of film thickness, *h*, on craze structure was first studied by transferring thickness gradients of polystyrene prepared by flow coating onto a copper grid and applying uniaxial strain (Figure 1). The crystallization morphology and kinetics of isotactic polystyrene were mapped previously using high-throughput techniques. By working in the same thickness range with amorphous gradients, pre- and post-strain crystallization could be used as a second gradient orthogonal to *h* after validation with the single gradient.

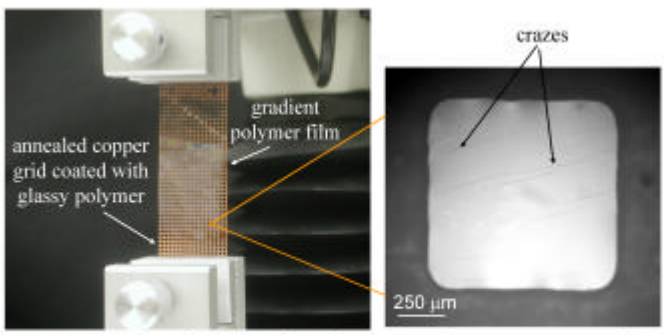

Figure 1: A gradient thickness film of isotactic polystyrene supported on a copper grid and mounted on a strain stage (left). An optical image of one grid square post-strain showing craze structures (right).

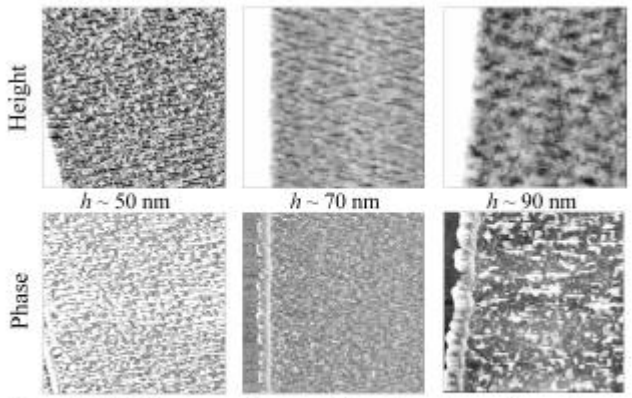

Figure 2: AFM images of craze mid-sections in various sub-regions of the film show variation in craze microstructure

After strain was applied, the grid was removed from the strain stage and regions of the crazes near the tip and midsection were imaged using AFM. The material inside the craze typically consists of threads or fibrils that span the width of the craze. It is the fibrils that provide mechanical strength to the craze prior to crack formation. Preliminary tests investigated a thickness range over which it was previously known that fibril diameter would increase with decreasing *h*. In the case of isotactic polystyrene, however, the lateral scale of the craze microstructure increased with decreasing *h* (Figure 2). Therefore, we are not observing fibril growth, but some other strain-induced ordering, perhaps crystallization.

One advantage of AFM over other techniques used to image craze microstructure such as TEM, is the ability to quantify craze depth and obtain phase information which can be correlated with the frictional coefficient of the surface. This has revealed a steady decrease in craze depth with film thickness and unexpected perforations along the wall of the craze, respectively. Future work includes comparison with non-crystalline, atactic polystyrene in the same thickness range and further quantitative analysis of the AFM data.

Contributors and Collaborators

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